



## Solving and refining crystal structures using symmetry mode crystallography: AMPLIMODES + FullProf.

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## Outline

- Overview of the *Symmetry Analysis* in phase transitions
- How is implemented the use of symmetry modes in *FullProf*
- Detailed example: Comparison of  $\text{CaTiO}_3$  and  $\text{LaMnO}_3$



## Symmetry and Phase Transitions

In a displacive phase transition the symmetry-breaking distortion (with respect to the high symmetry phase) is mainly caused by the freezing of the *primary mode*, associated with the order parameter.

In general, *secondary modes are also triggered at the transition* and can have non-zero amplitudes in the distorted structure.

The symmetry-mode analysis of a structural phase transition consists on the calculation of the amplitudes of the **symmetry modes frozen** in the distortion characterized by the **eigenvectors** of both primary and secondary modes present in the distortion.



## Symmetry and Phase Transitions

**Modes are collective correlated atomic displacements** fulfilling certain symmetry properties. Structural distortions can be decomposed into contributions from different modes with symmetries given by **irreducible representations** of the parent space group.

In general, the **use of symmetry-adapted modes** in the description of distorted structures introduces a **natural physical hierarchy among the structural parameters**. This can be useful not only for investigating the **physical mechanisms** that stabilize these phases, but also for **pure crystallographic purposes**.



## Mode Crystallography

The team of the Bilbao Crystallographic Server has developed the computer program: **AMPLIMODES**, that allows an easy calculation of the decomposition in modes of a distorted crystal structure with respect to a (virtual) high symmetry structure.

The originality of this approach with respect to more classical ones (e.g. BasIreps, MODY, Sarah, ...) is that the **polarization vectors are referred to the basis of the low symmetry phase**, allowing to use conventional crystallographic approaches (asymmetric unit and space group operators) to the crystal structure analysis.

AMPLIMODES: Symmetry mode analysis on the Bilbao Crystallographic Server, D. Ortoño, C. Capillas, M.I. Aroyo and J.M. Perez-Mato, *JApplCryst* **42**, 820 (2009)



## Distorted structures in terms of modes

Let  $\mathbf{r}(\mu)$  be the positions of the atoms  $\mu$  ( $\mu=1,\dots,s$ ) within an asymmetric unit of the parent structure with space group  $H$ . The asymmetric unit of the observed distorted structure with lower space group  $L$ , subgroup of  $H$ , will in general have a larger number of atoms due to the splitting of the Wyckoff orbits in  $H$ .

$$\mathbf{r}(\mu, i) = \mathbf{r}_0(\mu, i) + \mathbf{u}(\mu, i) \quad \mu = 1, 2, \dots, s, \quad i = 1, 2, \dots, n_\mu$$

$$\mathbf{u}(\mu, i) = \sum_{\tau, m} A_{\tau, m} \boldsymbol{\varepsilon}(\tau, m | \mu, i)$$

The indices  $\tau$  and  $m$  label all possible distinct allowed symmetry-adapted distortion modes.  $\tau$  stands for the possible different mode symmetries, while  $m$  ( $m=1,\dots,n_\tau$ ) enumerates the possible different independent modes of a given symmetry.

## Distorted structures in terms of modes

$$\mathbf{u}(\mu, i) = \sum_{\tau, m} A_{\tau, m} \boldsymbol{\varepsilon}(\tau, m | \mu, i) \quad \mu = 1, 2, \dots, s, \quad i = 1, 2, \dots, n_\mu$$

The mode  $(\tau, m)$  is defined by the polarisation vectors:

$$\boldsymbol{\varepsilon}(\tau, m | \mu, i)$$

One can refer to the global polarization vector  $\boldsymbol{\varepsilon}(\tau, m)$ , taking all atoms simultaneously, of the mode  $(\tau, m)$

The displacements of an atom  $(\mu, i)$  related by the symmetry operator  $\{\mathbf{R}|t\}$  to the atom  $(\mu, i)$  are given directly by:

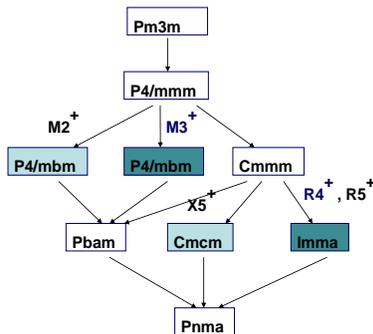
$$\mathbf{u}(\mu', i') = \mathbf{R} \mathbf{u}(\mu, i) = \sum_{\tau, m} A_{\tau, m} \mathbf{R} \boldsymbol{\varepsilon}(\tau, m | \mu, i)$$

## Distorted structures in terms of modes

The distortion modes of the phase with group H having **isotropy group** equal to L can be called **primary**, while those with **isotropy groups** given by **subgroups** of H which are distinct **supergroups** of L, are usually termed **secondary**.

A **primary distortion mode** is sufficient to produce the observed symmetry breaking between the **parent** and the **observed** structure, while **secondary distortion modes** alone would yield a **higher symmetry**.

### Group-subgroup chains relating $Pm3m$ and $Pnma$



## Distorted structures in terms of modes

The normalization of the polarisation vectors is chosen to verify:

$$\sum_{\mu, i} mult_{\mu, i} |\boldsymbol{\varepsilon}(\tau, m | \mu, i)|^2 = 1$$

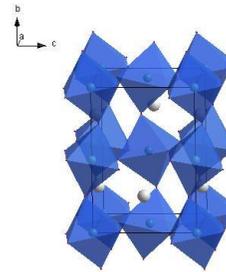
" $mult_{\mu, i}$ " represents the multiplicity in a primitive cell of the space group L for the Wyckoff position  $(\mu, i)$ .

The following orthogonality relation is verified by the polarization vectors:

$$\sum_{\mu, i} mult_{\mu, i} \boldsymbol{\varepsilon}(\tau, m | \mu, i) \boldsymbol{\varepsilon}(\tau', m' | \mu, i) = \delta_{\tau\tau'} \delta_{mm'}$$

### Distorted perovskite: structure type $GdFeO_3$

Space group:  $Pnma$ , parent structure  $Pm3m$



## Distorted structures in terms of modes

It is also in general very convenient to express the global distortion in terms of the **different symmetry components** (this is done in AMPLIMODES):

$$\mathbf{u}(\mu, i) = \sum_{\tau, m} A_{\tau, m} \boldsymbol{\varepsilon}(\tau, m | \mu, i) = \sum_{\tau} A_{\tau} \boldsymbol{\varepsilon}(\tau | \mu, i)$$

$$A_{\tau} = \left( \sum_m A_{\tau, m}^2 \right)^{1/2}$$

$$\boldsymbol{\varepsilon}(\tau | \mu, i) = \sum_m a_{\tau, m} \boldsymbol{\varepsilon}(\tau, m | \mu, i); \quad a_{\tau, m} = \frac{A_{\tau, m}}{\left( \sum_m A_{\tau, m}^2 \right)^{1/2}}$$

NEUTRONS FOR SCIENCE **Outline**

➔ Overview of the *Symmetry Analysis* in phase transitions

➔ How is implemented the use of symmetry modes in *FullProf*

➔ Detailed example: Comparison of CaTiO3 and LaMnO3

NEUTRONS FOR SCIENCE **Refinement of crystal structures using amplitudes of symmetry modes instead of atom positions in FullProf**

In *FullProf* the refinement of a crystal structure can be done in terms of symmetry adapted modes.  
<http://www.ill.eu/sites/fullprof/>

*FullProf* uses the polarisation vectors obtained from the output of the program **AMPLIMODES** from the Bilbao Crystallographic Server

<http://www.cryst.ehu.es/cryst/amplimodes.html>

A low symmetry (LS) crystal structure (Space Group L) is supposed to derive (from a phase transition) from a high symmetry (HS) structure (Space Group H) with  $L \subset H$ .

The free parameters, instead of atom positions, are the amplitudes of a combination of allowed symmetry modes.

NEUTRONS FOR SCIENCE **Refinement of crystal structures using amplitudes of symmetry modes instead of atom positions in FullProf**

The atoms position are calculated from the following formula:

$$\mathbf{r}_j^{LS} = \mathbf{r}_j^{HS} + \sum_m c_m Q_m \boldsymbol{\varepsilon}(m|j)$$

Where  $j$  runs over the atoms in the asymmetric unit of the LS phase  
 The index  $m$  runs over all contributing modes. It may content modes corresponding to different representations and wave vectors of the H space group (Isotropy subgroups) that are compatible with the L space group.

The polarisation vectors  $\boldsymbol{\varepsilon}(m|j)$  have normalized components referred to the conventional cell of the LS phase and are provided by **AMPLIMODES**. The refined parameters are the amplitudes  $Q_m$ ,  $c_m$  are normalisation coefficients.

A representation of the modes using arrows and the HS phase can be visualised using **FullProf Studio**

**Example of PCR file for FullProf corresponding to the compound LaMnO3**

```
LaMnO3
!
!Nat Dis Ang Pr1 Pr2 Pr3 /Jbt Trf Isy Str Furth ATZ Nvk Npr More
4 0 0 0.0 0.0 1.0 6 0 0 0 7 967.370 0 7 1
P b n m <--Space group symbol
!Atom Typ X Y Z Biso Occ
La LA 0.00000 0.50000 0.25000 0.35050 0.50000
0.00 0.00 0.00 251.00 0.00
Mn MN 0.00000 0.00000 0.00000 0.21228 0.50000
0.00 0.00 0.00 261.00 0.00
O1 O 0.75000 0.25000 0.00000 0.43965 1.00000
0.00 0.00 0.00 271.00 0.00
O2 O 0.50000 0.50000 0.75000 0.50234 0.50000
0.00 0.00 0.00 271.00 0.00
! Polarisation Vectors of symmetry modes for each atom
V_MODES 12
! Nm Atm Irrep Vx Vy Vz Coeff
1 O1 R4+ 0.000000 0.000000 0.031721 1.000000
1 O2 R4+ 0.063442 0.000000 0.000000 1.000000
2 La R5+ -0.089721 0.000000 0.000000 1.000000
3 O1 R5+ 0.000000 0.000000 -0.031721 1.000000
. . . . .
7 O2 M3+ 0.000000 0.000000 0.000000 1.000000
! Amplitudes of Symmetry Modes
```

NEUTRONS FOR SCIENCE **Example of PCR file for FullProf corresponding to the compound LaMnO3**

```
! Polarisation Vectors of Symmetry Modes for each atom
V_MODES 12
! Nm Atm Irrep Vx Vy Vz Coeff
1 O1 R4+ 0.000000 0.000000 0.031721 1.000000
1 O2 R4+ 0.063442 0.000000 0.000000 1.000000
2 La R5+ -0.089721 0.000000 0.000000 1.000000
3 O1 R5+ 0.000000 0.000000 -0.031721 1.000000
. . . . .
7 O2 M3+ 0.000000 0.000000 0.000000 1.000000
! Amplitudes of Symmetry Modes
A_MODES 7 1 1 1 1 1 1
Q1_R4+ -1.189680 181.0000
Q2_R5+ -0.086467 191.0000
Q3_R5+ 0.018171 201.0000
Q4_X5+ -0.546082 211.0000
Q5_X5+ -0.139910 221.0000
Q6_M2+ 0.355652 231.0000
Q7_M3+ 0.901264 241.0000
!-----> Profile Parameters for Pattern # 1
! Scale Shapel Bvov Str1 Str2 Str3 Strain-Model
0.86919E-01 0.00000 0.00000 0.0000 0.0000 0.0000 0
```

NEUTRONS FOR SCIENCE **Visualisation of single modes using FullProf Studio**

- A part from the normal FST file generated normally for the final crystal structure, **FullProf** outputs a series of FST files containing
- The “virtual structures” corresponding to single modes (e.g. A\_MODES 7 0000000)
- A representation of the high symmetry phase together with arrows indicating the displacement of atoms in the corresponding mode: (e.g. A\_MODES 7 1111111)
- Both kinds of representations depending on the mode (e.g. A\_MODES 7 1001101)

The items after the number of modes are:  
 $p\_mode(i) \quad i=1, \dots, n\_modes$

## Visualisation of Irreps modes using FullProf Studio

If the value of `p_mode(1)=2` (see note of 29 August 2008 in `fp2k.inf`) the other values are not needed.

The program interprets this value as an indication to output in the FST and OUT files the structures corresponding to single irreducible representations (Irreps).

All modes corresponding to a single Irrep are combined in the FST file.

## Visualisation of modes using FullProf Studio: Summary

### Examples:

`A_MODES 7 7` → All the 7 independent modes are represented by displacement vectors (arrows)

`A_MODES 7 -7` → All the 7 independent modes are represented by virtual distorted structures

`A_MODES 7 -3` → No output of independent modes in FST files

## Visualisation of single modes using FullProf Studio

### Examples:

`A_MODES 7 2` → Modes regrouped in an FST file per irreducible representation (arrows, default of AMPLIMODES)

`A_MODES 7 -2` → Modes regrouped in an FST file per irreducible representation (structures)

`A_MODES 7 1110110` → Explicit output of all modes (1: arrows, 0: distorted structure)

## Visualisation of single modes using FullProf Studio

### Examples:

`A_MODES 7 4 1 3 -4 7` → Only the 4 modes 1,3,4 and 7 are output in FST files. All of them, except the mode 4, are represented by arrows.

## Outline

- Overview of the *Symmetry Analysis* in phase transitions
- How is implemented the use of symmetry modes in *FullProf*
- Detailed example: the case of  $\text{CaTiO}_3$  and comparison with  $\text{LaMnO}_3$

## AMPLIMODES: Bilbao Crystallographic Server

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**AMPLIMODES for FullProf**

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**AMPLIMODES for FullProf**

K-vector	Irrep	Direction	Isotropy Subgroup	Dimension
(1/2, 1/2, 1/2)	R4+	(-a,a,0)	Imma (74)	1
(1/2, 1/2, 1/2)	R5+	(a,a,0)	Imma (74)	2
(0, 1/2, 0)	X5+	(a,0,0,0,0)	Cmcm (63)	2
(1/2, 1/2, 0)	M2+	(0,0,a)	P4mbm (127)	1
(1/2, 1/2, 0)	M3+	(0,0,a)	P4mbm (127)	1

### AMPLIMODES for FullProf

Text to be copied in the PCR file and button "here" to create a template of PCR file for calculations with FullProf

### AMPLIMODES for FullProf: Template of PCR file

### Running FullProf with the PCR file generated by AMPLIMODES

- 1: Select, in the "File" menu the working directory
- 2: Load the PCR file in toolbar (first left button). In our case the file is called: **bcs\_template\_cti.pcr**
- 3: The file can be readily edited by clicking on the second button and eventually modified
- 4: Clicking on the "FullProf" button, the program runs and produces files that may be inspected or used for plotting the calculated diffraction pattern and the crystal structure.

### Running FullProf with the PCR file generated by AMPLIMODES

Calculation done for a cubic ideal perovskite described in the low symmetry setting

### Running FullProf with the PCR file generated by AMPLIMODES

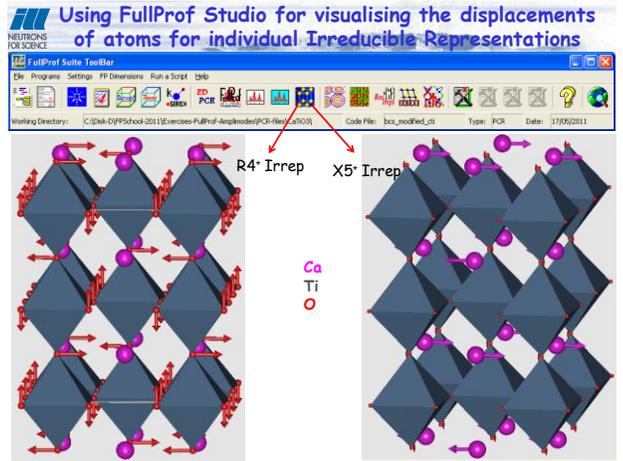
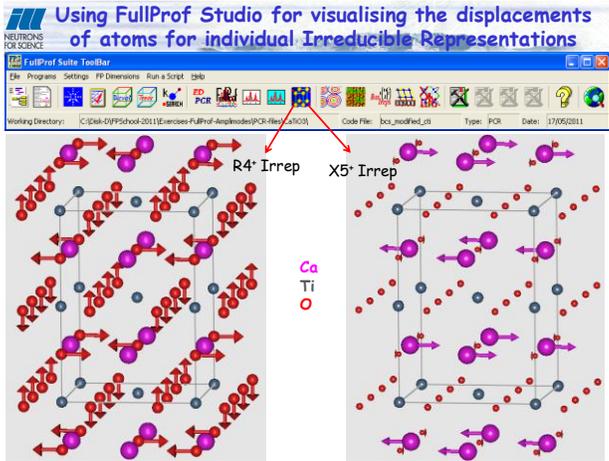
The calculation is done for a cubic ideal perovskite described in the low symmetry setting. One can edit the file, write the real unit cell parameters and add arbitrary reasonable values to the amplitudes (in angstroms) to see the modification of the powder pattern (let us call the PCR file: **bcs\_modified\_cti.pcr**).

For instance, introducing the following values:

- A1\_R4+ 0.800000 1.00
  - A2\_R5+ -0.100000 1.00
  - A3\_R5+ 0.300000 1.00
  - A4\_X5+ 0.700000 1.00
  - A5\_X5+ 0.100000 1.00
  - A6\_M2+ 0.020000 1.00
  - A7\_M3+ 0.100000 1.00
- a= 5.441Å, b=7.645 Å, c=5.380 Å

### Running FullProf with the PCR file generated by AMPLIMODES and modified by the user

Calculation done for the distorted structure with the amplitudes given above and using the real cell parameters



### WinPLOTR 2006 Version: 0.50

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load

After loading the file into WinPLOTR-2006, the first step is to select background points in a file. The procedure is indicated in the following three slides.

### Preparing a PCR file for treating real data: Background selection

### Preparing a PCR file for treating real data: Background selection

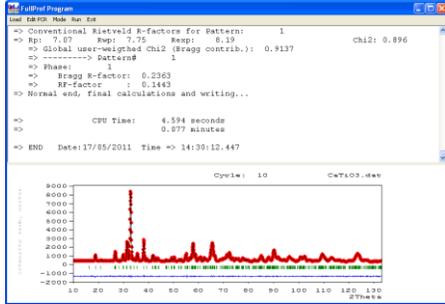
### Preparing a PCR file for treating real data: Background selection





### Le Bail Fit on CaTiO<sub>3</sub> data after convergence. UVWY and cell parameters have been refined

Putting now Aut=1 and setting to 1 the codes of the parameters to be refined (cell parameters and profile parameters U,V,W and Y) we re-run the program again. After convergence, FullProf gives the result below.



### Preparing a simulated annealing PCR file for working with integrated intensity clusters of CaTiO<sub>3</sub> (1)

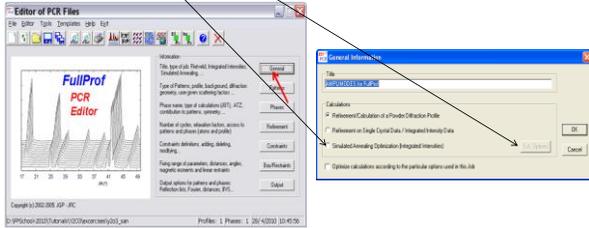
Copy the modified file (with the real cell parameters) from the BCS into another one

Example.  
If the initial file is called **bc\_s\_modified\_cti.pcr**  
The new file will be called **cti\_san.pcr**

Load **cti\_san.pcr** in the toolbar and click on **EdPCR** button. The file is loaded into **EdPCR** and we are prepared for modifications.

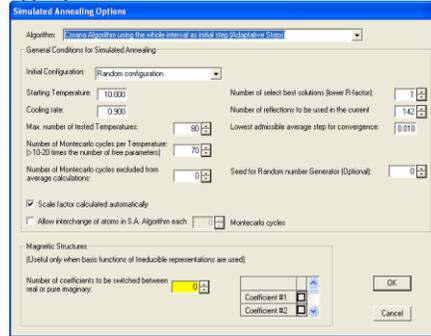
### Preparing a simulated annealing PCR file for working with integrated intensity clusters of CaTiO<sub>3</sub> (2)

Tick the "Simulated Annealing Optimisation (Integrated Intensities)" item and then click on the "S.A. Options" button.



### Preparing a simulated annealing PCR file for working with integrated intensity clusters of CaTiO<sub>3</sub> (3)

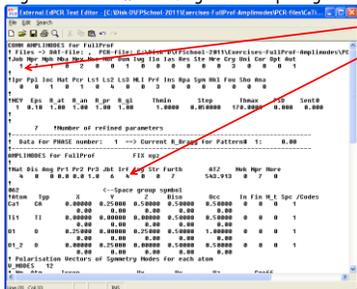
The following dialog opens and the user has to fill the appropriate boxes. The shown values are OK for CaTiO<sub>3</sub> case.



Clicking on OKs returns to the general interface.

### Preparing a simulated annealing PCR file for working with integrated intensity clusters of CaTiO<sub>3</sub> (4)

Select the menu: Editor → Unsaved Input File to open the unsaved.pcr file and change by hand Job to 1 (experimental neutron data) and Irf to 4 (integrated intensities provided for the phase). Save the file giving it the name **cti\_san.pcr** to replace the original and then reopen (clicking on "Yes" button) the changed file into EdPCR. Save again to provoke EdPCR to generate automatic changes and reopen again the internal editor to continue.



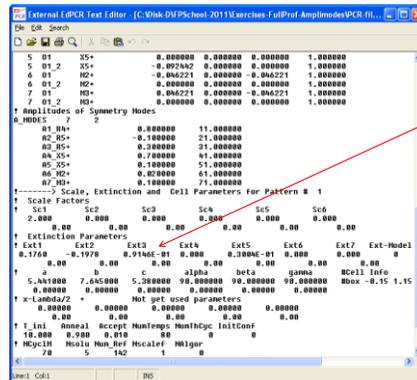
Put **Job=1** and **Irf=4** and save the file giving it the name **cti\_san.pcr**



Click yes and re-save the file again for making automatic changes in the file

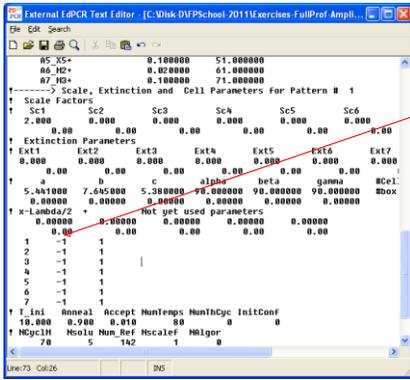
### Preparing a simulated annealing PCR file for working with integrated intensity clusters of CaTiO<sub>3</sub> (5)

Within EdPCR, accessing the menu : Editor → Input Control File (.PCR) Edit the file and delete superfluous items. In particular put to zero all Ext1 items, that were imported from previous U,V,W parameters.



Notice that the amplitudes have now refinement codes. There are 7 free parameters and one has to introduce the box conditions for variations of amplitudes.

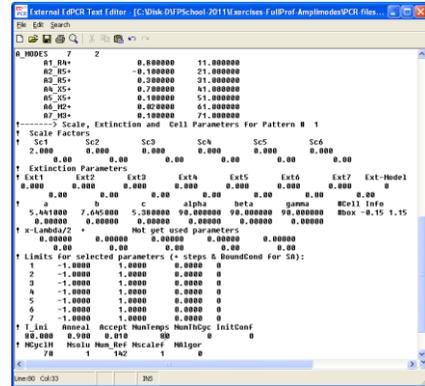
**Preparing a simulated annealing PCR file for working with integrated intensity clusters of CaTiO<sub>3</sub> (6)**



Modify the value of **Nre** on top of the file to the value **7 (Nre=7)**, not shown in the figure.

Add seven lines, at the indicated position, starting with the numbers 1, 2 ... 7 and put -1 in the same lines to tell the program that the parameter numbered as 1, 2 ... may vary between -1 and 1. We do not allow variations of amplitudes bigger than one angstrom. Save, re-open the file and save again as before.

**Preparing a simulated annealing PCR file for working with integrated intensity clusters of CaTiO<sub>3</sub> (7)**

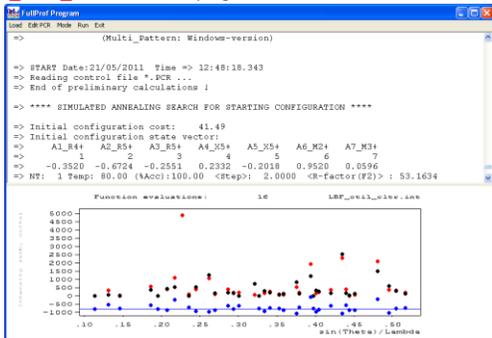


Within EdPCR, editing again → **Input Control File (.PCR)**  
Verify that the aspect of the file is similar to that we have in the picture

Now the file is prepared to run FullProf in simulated annealing mode using Clusters of Integrated Intensities.

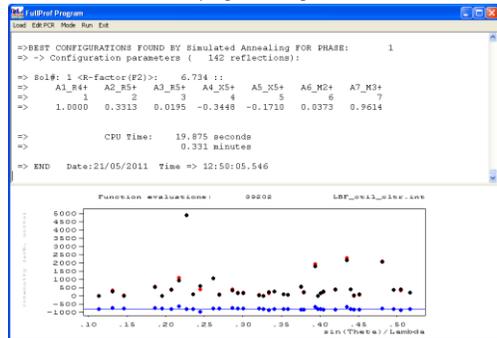
**Running a simulated annealing job with integrated intensity clusters of CaTiO<sub>3</sub>**

Having the created file **cti\_san.pcr** loaded in the FPS toolbar, one can run FullProf and select as intensity file **LBF\_ctil\_cltr.int**. The program launches as shown below



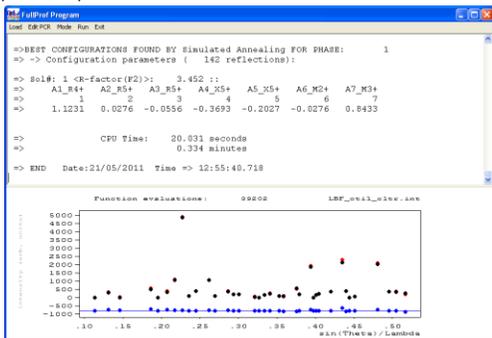
**Running a simulated annealing job with integrated intensity clusters of CaTiO<sub>3</sub>**

One can see that one of the amplitudes is blocked at the value 1.0, this means that we have to enlarge the limits in order to allow larger values. We can re-run the program using different constraints.



**Running a simulated annealing job with integrated intensity clusters of CaTiO<sub>3</sub>**

This is another run in which we have increased the range of amplitudes up to 1.3Å.



**Results of the simulated annealing (SAN) run on CaTiO<sub>3</sub> data**

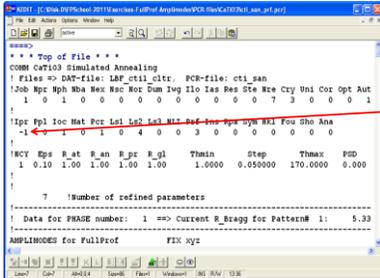
We have seen that the results depend of the constraints. When the maximum amplitude was limited to 1, the results were worse and freeing these conditions the R-factor diminished. When compared with the results of the Least Squares (LSQ) refinement done above, we see that the good order of magnitude is obtained. Keep in mind that we have used only a part of the diagram and clusters of integrated intensities. The SAN method is normally used for solving a structure and get initial values of parameter for a further treatment using LSQ.

Comparison of LSQ and SAN amplitudes

Name	Value	Simulated (Integrated Amplitudes)
A1_R4+	1.110 (3)	1.1231
A2_R5+	0.065 (7)	0.0276
A3_R5+	-0.031 (5)	-0.0556
A4_X5+	-0.386 (4)	-0.3693
A5_X5+	-0.173 (3)	-0.2027
A6_M2+	0.008 (3)	-0.0276
A7_M3+	0.853 (4)	0.8433

### Simulated annealing (SAN) using profile intensities on CaTiO<sub>3</sub> data

When the structure is more complex and we need to overcome as much as possible the problem of overlap, one can use the profile intensities instead of integrated intensity clusters. For that it suffices to put **Ipr=-1**, as shown below. Remember that we already prepared the output of the information needed for this option, when we put **Ipr=-1** in the LBF method.



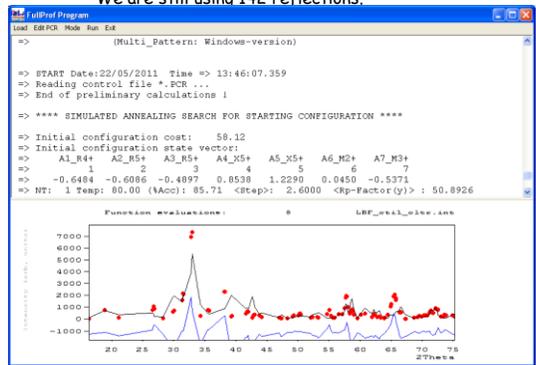
Copy the file **cti\_san.pcr** into the file **cti\_san\_spr.pcr**.

Edit the last file and change to **Ipr=-1**.

Rename the file **LBS\_cti\_spr** into **cti\_san\_spr.pcr**

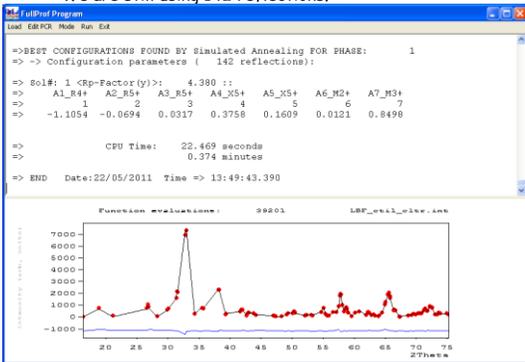
### Simulated annealing (SAN) using profile intensities on CaTiO<sub>3</sub> data

Start of the profile intensity SAN job. We are still using 142 reflections.



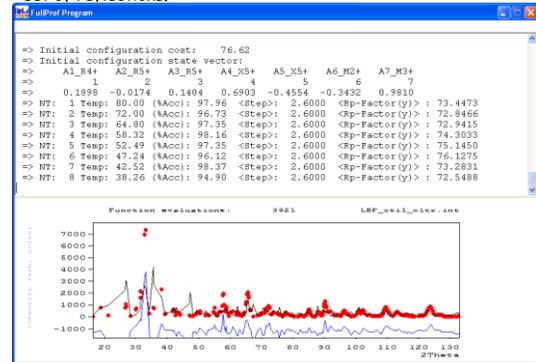
### Simulated annealing (SAN) using profile intensities on CaTiO<sub>3</sub> data

Final picture of the profile intensity SAN job. We are still using 142 reflections.



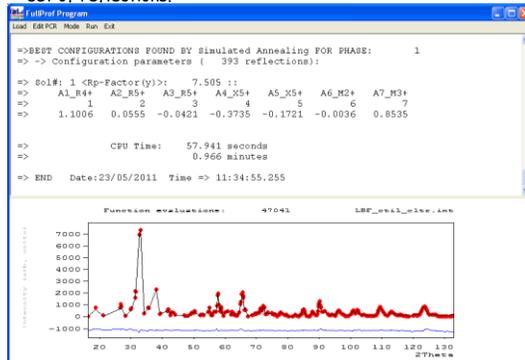
### Simulated annealing (SAN) using profile intensities on CaTiO<sub>3</sub> data

Starting part of the profile intensity SAN job using the full set of reflections.



### Simulated annealing (SAN) using profile intensities on CaTiO<sub>3</sub> data

Final picture of the profile intensity SAN job using the full set of reflections.



### Comparison of Simulated annealing jobs on CaTiO<sub>3</sub>

We compare below the values of LSQ and different SAN jobs.

Comparison of LSQ and SAN amplitudes for CaTiO<sub>3</sub>

Least squares refinement Name	Value	Simulated Annealing (Integrated Intensities)	Simulated Annealing (Profile Intensities)
A1_R4+	1.110 (3)	1.1231	1.1006
A2_R5+	0.065 (7)	0.0276	0.0555
A3_R5+	-0.031 (5)	-0.0556	-0.0421
A4_X5+	-0.386 (4)	-0.3693	-0.3735
A5_X5+	-0.173 (3)	-0.2027	-0.1721
A6_M2+	0.008 (3)	-0.0276	-0.0036
A7_M3+	0.853 (4)	0.8433	0.8535



### Comparing $\text{CaTiO}_3$ and $\text{LaMnO}_3$

In this tutorial we provide also neutron powder diffraction data for  $\text{LaMnO}_3$ . For this compound we can repeat exactly the same steps as for  $\text{CaTiO}_3$  and do the symmetry mode analysis in the same way. The most important difference between the two structures is the presence of a strong component of the  $M2+$  mode corresponding to the active Jahn-Teller effect in  $\text{LaMnO}_3$ . In the following we show the value of the amplitudes of the five irreps in both compounds.

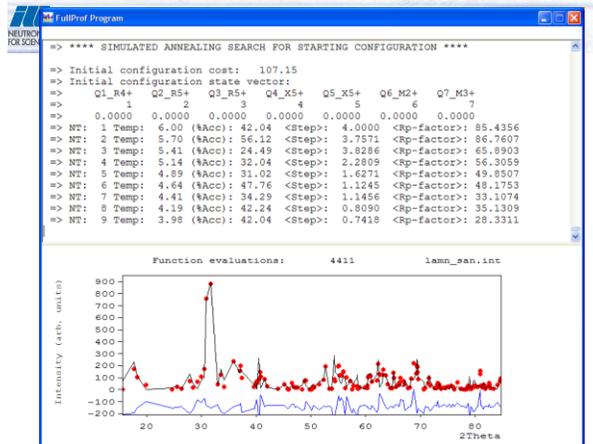
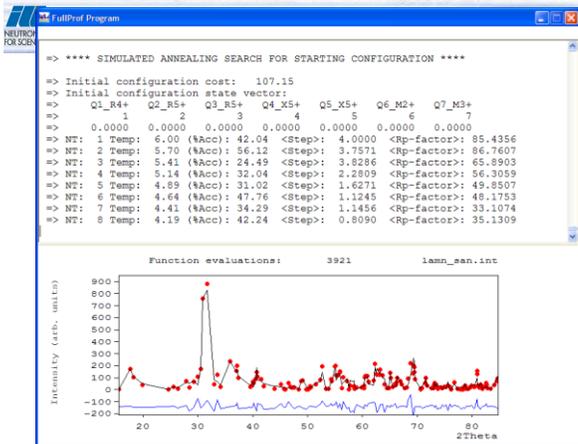
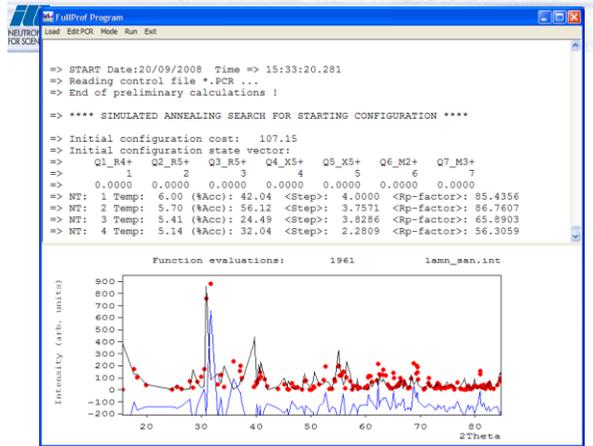
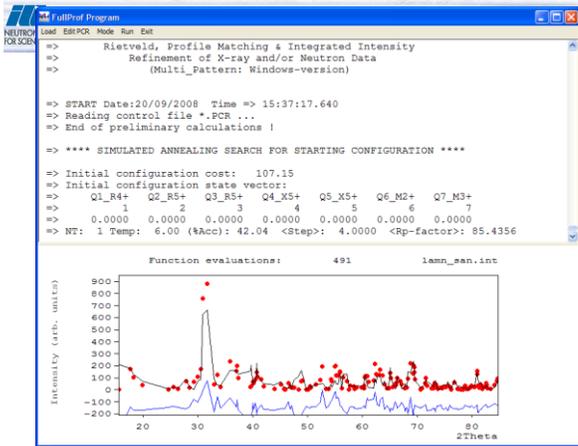
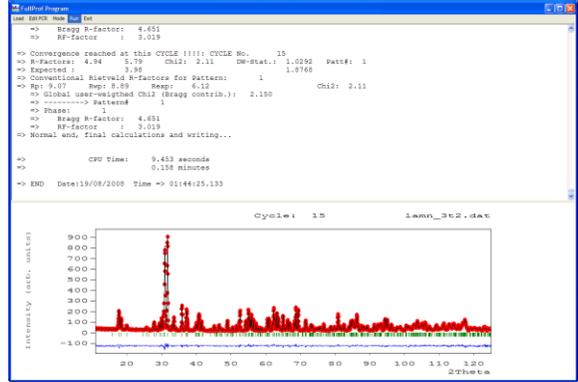
Comparison of LSQ amplitudes of  $\text{CaTiO}_3$  and  $\text{LaMnO}_3$

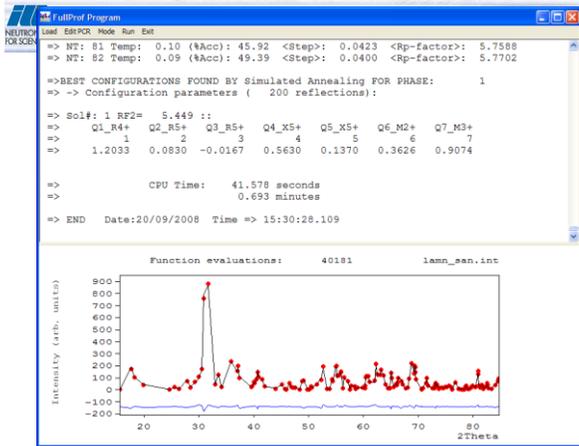
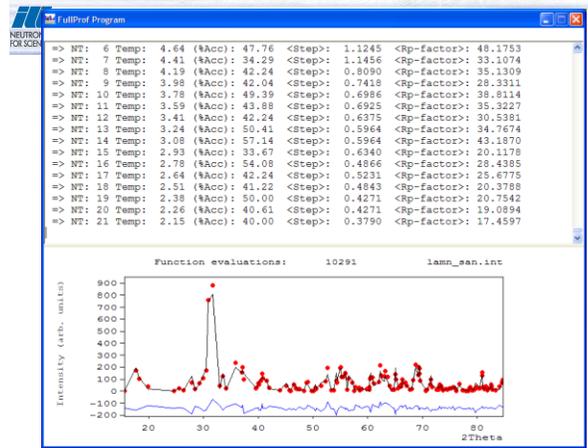
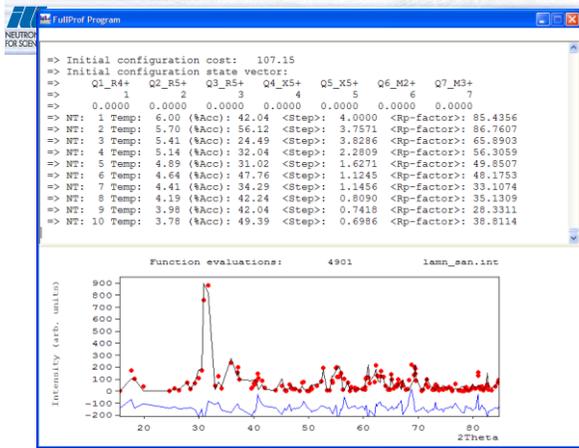
	$\text{CaTiO}_3$	$\text{LaMnO}_3$
A1_R4+	1.110 (3)	1.195 (3)
A2_R5+	0.065 (7)	0.084 (2)
A3_R5+	-0.031 (5)	-0.019 (3)
A4_X5+	-0.386 (4)	-0.546 (2)
A5_X5+	-0.173 (3)	-0.141 (3)
A6_M2+	0.008 (3)	-0.363 (3)
A7_M3+	0.853 (4)	0.904 (3)

In the following slides we show the running of a LSQ refinement and a profile intensity SAN run for  $\text{LaMnO}_3$ , as well as a series of pictures of the crystal structure and symmetry modes.

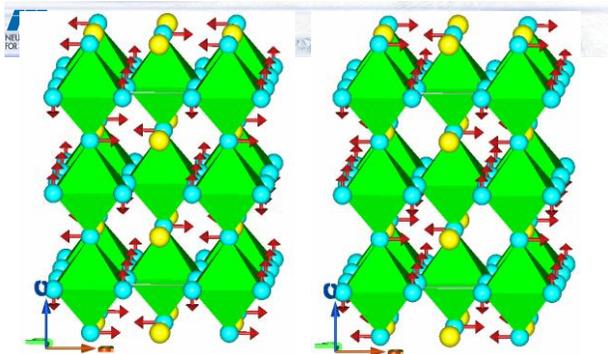
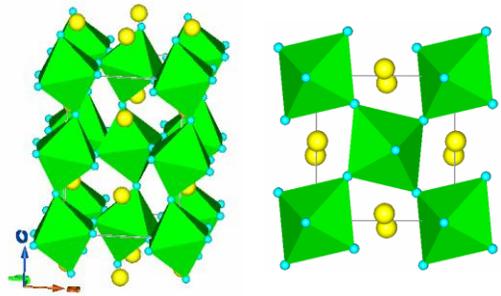


### Example of FullProf running a LSQ refinement of $\text{LaMnO}_3$ using symmetry modes



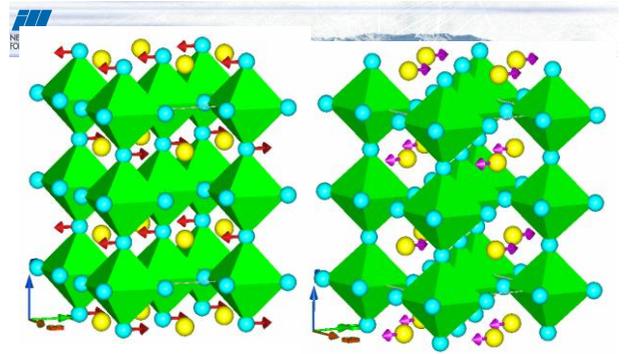


## Crystal Structure of LaMnO<sub>3</sub>



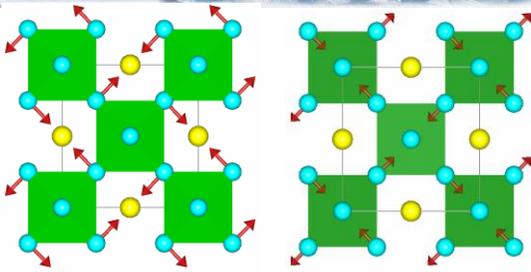
Mode 1, Q1\_R4+ = -1.18968  
O1 R4+ (0.0, 0.0, 0.031721)  
O2 R4+ (0.063442, 0.0, 0.0)

Mode 3, Q3\_R5+ = 0.018171  
O1 R5+ (0.0, 0.0, -0.031721)  
O2 R5+ (0.063442, 0.0, 0.0)



Mode 5, Q5\_X5+ = -0.139910  
O2 X5+ (0.0, -0.089721, 0.0)

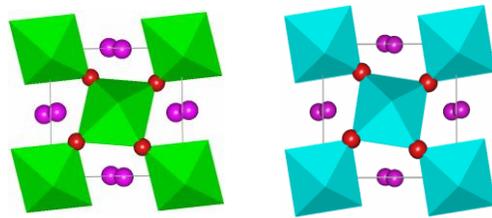
Mode 4, Q4\_X5+ = -0.546082  
La X5+ (0.0, -0.089721, 0.0)



Mode 7, Q7\_M3+ = 0.901264  
 O1 M3+ (-0.04486, -0.04486, 0.0)

Mode 6, Q6\_M2+ = 0.355652  
 O1 M2+ (0.04486, -0.04486, 0.0)

### Comparison of the crystal structures of $\text{LaMnO}_3$ and $\text{CaTiO}_3$



Pictures (seen along [010]) of the crystal structures of  $\text{LaMnO}_3$  (left panel) and  $\text{CaTiO}_3$  (right panel) showing the stronger distortion of  $\text{MnO}_6$  octahedra in comparison with  $\text{TiO}_6$  octahedra due to the Jahn-Teller effect that is active in  $\text{LaMnO}_3$ . The antiferro-distorsive orbital ordering is clearly seen as an elongation of the occupied  $d_{3z^2}$ -like orbital. This corresponds to a Mn-O distance that is much longer than the others ( $d_z=1.904(1)$ ,  $d_{xy}=1.969(2)$ ,  $d_{xz}=2.182(1)$ ). The short and long distances are nearly within the shown  $ab$  plane and a long bond is always connected to the short bond of the adjacent octahedra.